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## PATENT SPECIFICATION

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1,116,927

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The Inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:—HEINZ BILLE, HARRO PETERSEN and WILHELM RUEMENS, citizens of the Federal Republic of Germany, residing, respectively, at 1 b Eschkopfstrasse, Limburgerhof/Pfalz; Germany, 17 Augusta-Anlage, Mannheim; Germany, and 35 Hardenburgstrasse, Limburgerhof/Pfalz; Germany.

## COMPLETE SPECIFICATION

## Finishing Cellulosic Fibrous Materials

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that cellulosic fibrous materials (i.e. fibrous materials consisting of or containing cellulose) may be finished by impregnating them with aqueous solutions or dispersions of cross-linkers, i.e. low molecular weight substances which contain at least two N-methylol groups and/or N-methylol ether groups, and acid or potentially acid catalysts and then reacting the N-methylol groups and/or N-methylol ether groups with each other, with other groups of the substances bearing them, and/or with the cellulose.

The purpose of this treatment is mainly to reduce the tendency of cellulose to crease. Reaction of the N-methylol groups and N-methylol ether groups is usually carried out by drying the impregnated fibrous material and heating it to a temperature of up to 160°C. In this way dry crease angles and wet crease angles are obtained having the same order of magnitude, and their size could be adapted to all requirements were it not for the fact that the higher the dry crease angle, the smaller the ultimate tensile strength of the treated material.

It has therefore been recommended to carry out the abovementioned reaction without drying on the swollen fibrous material. In this way it is possible to achieve a marked increase in the wet crease angle without too much loss of tensile strength, but the dry crease angle is not improved and satisfactory behavior of the treated material in use is not ensured.

According to more recent knowledge, the maximum value in use is achieved when a high wet crease angle and a medium dry crease angle are imparted to the fibrous material with only slight damage to the fiber. To achieve this result it has hitherto been necessary to carry out finishing in the swollen condition and finishing in the dry condition in a two-stage process. Although attempts have been made to achieve the same result in a one-stage process by treating the fibrous material with formaldehyde and drying it carefully at low temperatures, the process is so difficult to control that reproducible effects can hardly be obtained. Up to now there has been no single-stage process for the achievement of high wet crease angles and medium dry crease angles which is simple and reliable in operation.

[Price 4s. 6d.]

It is an object of the present invention to finish cellulosic fibrous material in one operation so that it has high to very wet crease recovery and medium dry crease recovery.

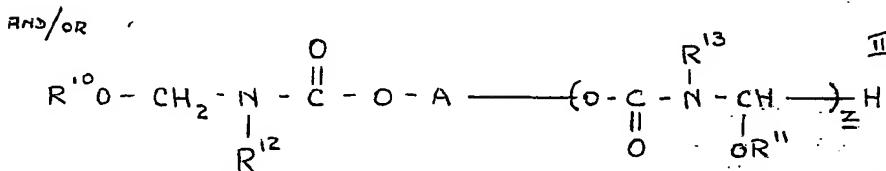
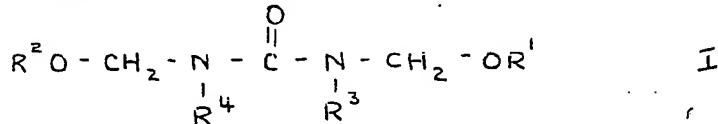
5 A further object of the invention is to finish cellulosic fibrous material so that in addition to good crease recovery it has particularly good abrasion resistance and tensile strength. Yet another object of the invention is to finish fibrous material of the said type in a particularly reliable way and with reproducible results.

10 These and other objects are achieved by the invention. We have found that cellulosic fibrous material can be finished in one operation in a particularly simple and mild manner so that it has a high wet crease angle and a medium dry crease angle by impregnating the material to be finished with an aqueous solution or dispersion which contains as crosslinking agent at least one monomeric compound which bears 15 at least two groups having the formula  $-\text{CH}_2-\text{OR}$  (in which R denotes a hydrogen atom or a low molecular weight alkyl radical) attached to the nitrogen atom of a carbamide group, and as catalyst a water-soluble catalyst comprising a mixture of:

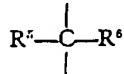
(a) at least one strong or medium-strength acid which is not volatile at temperatures up to  $130^\circ\text{C}$  and

(b) at least one potentially acid salt, the ratio by weight of (a) to (b) being from 1:10 to 5:1, drying the impregnated 20 material to a moisture content of the cellulose of 10 to 35% by weight, with reference to the weight of the amorphous regions contained in the cellulose, and allowing it to react with the applied crosslinking agent at a temperature of up to  $50^\circ\text{C}$ , preferably from  $15^\circ$  to  $35^\circ\text{C}$ .

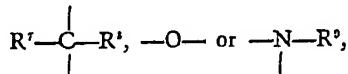
The substances having the formula:—



are particularly preferred as crosslinking agents, in which z denotes zero or 1;  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^{10}$  and  $\text{R}^{11}$  denote hydrogen atoms or low molecular weight alkyl groups;  $\text{R}^3$  and  $\text{R}^4$  denote radicals having the formula



30 which are connected with each other directly or via radicals



or when  $\text{R}^1$  and  $\text{R}^2$  denote low molecular weight alkyl radicals may also denote 35 hydrogen atoms, low molecular weight alkyl groups or low molecular weight alkoxy-methyl groups;  $\text{R}^5$  and  $\text{R}^7$  denote hydrogen atoms;  $\text{R}^6$  and  $\text{R}^8$  denote hydrogen atoms, hydroxyl groups, low molecular weight alkyl groups or low molecular weight 40 alkoxyl groups;  $\text{R}^9$  denotes a hydrogen atom, a low molecular weight alkyl group or a low molecular weight hydroxyalkyl group;  $\text{R}^{12}$  denotes a hydroxymethyl group or a low molecular weight alkoxyethyl group if z is zero, and a hydrogen atom, a hydroxymethyl group or a low molecular weight alkoxyethyl group if z is 1,  $\text{R}^{13}$  denotes a hydrogen atom, a hydroxymethyl group or a low molecular weight alkoxy-methyl group, and A denotes a divalent aliphatic hydrocarbon radical having two to eight carbon atoms.

By the term "low molecular weight" as applied to alkyl, hydroxyalkyl, alkoxy and alkoxyethyl groups, it means a group containing 1 to 4 carbon atoms in the alkyl portion.

5 By the term "carbamide group" is meant a group of the formula  $\text{---N---C=O}$ .

By the term "strong or medium-strength acid" is meant an acid whose dissociation constant (or first dissociation constant in the case of a polybasic acid) is at least  $10^{-4}$ .

Where radicals R are commonly defined, they may be identical or different.

Examples of substances having the formula I are: derivatives of urea, mono-

10 alkylureas and symmetrical dialkylureas containing at least 2 low molecular weight alkoxyethyl groups, such as N,N' - dimethoxymethylurea, N,N' - dibutoxy-

methyl - N - methyl - urea, N,N',N' - trimethoxymethyl - N - ethylurea and N,N' - diethoxymethyl - N,N' - dimethylurea, N,N' - dihydroxymethyl derivatives and low molecular weight N,N' - dialkoxyethyl derivatives of N,N' - ethylenurea

(=imidazolidone - 2), N,N' - 1,2 - propylenurea (=4 - methylimidazolidone - 2), N,N' - 1,3 - propylenurea (=N,N' - trimethylenurea or hexahydropyrimidone - 2),

15 5 - hydroxyhexahydropyrimidone - 2, hexahydro - 1,3,5 - triazine - 2 and its 5 - alkyl and 5 - hydroxyalkyl derivatives having up to four carbon atoms in the alkyl or hydroxyalkyl radicals, glyoxal monoureine (=4,5 - dihydroxyimidazolidone - 2) and urones. Examples of substances having the formula II are the hydroxymethyl

20 derivatives and the low molecular weight alkoxyethyl derivatives of monocarbamic and dicarbamic esters (=monourethanes and diurethanes), such as ethyl carbamate (urethane in the narrower sense), propyl carbamate, butyl carbamate, octyl carbamate and dicarbamic esters of ethylene glycol, 1,3 - butanediol, 1,4 - butanediol and 1,6 - hexanediol.

25 It is preferred to use N,N' - dihydroxymethyl and N,N' - dimethoxy-

methyl compounds of ethylenurea (=imidazolidone - 2), of 4,5 - dihydroxy-

30 hexahydro - 1,3,5 - triazine - 2 and of unsubstituted urone; N,N' - dimethoxy-

methylurea, N,N - dimethoxymethyl ethylurethane, N,N' - dihydroxymethylbutane-

diol - 1,4 - diurethane and N,N,N',N' - tetrahydroxymethylbutanediol - 1,4 -

diurethane have also proved to be very suitable.

A very important feature of the process according to this invention is the use of a combination of (a) at least one acid and (b) at least one potentially acid salt-type curing catalyst. By acid catalysts we mean free medium-strength or strong acids which are not volatile up to 130°C at atmospheric pressure, for example sulfuric acid, phosphoric acid, oxalic acid, glycolic acid, maleic acid, monochloroacetic acid, trichloroacetic acid, tartaric acid and citric acid. Oxalic acid, maleic acid and mixtures of the two have proved to be particularly suitable for the process according to this invention.

40 It is known that potentially acid salt-type catalysts are salts which per se have little or no acidity but by hydrolysis or thermal influence will liberate such an amount of acid that the reaction between cellulose and N-methylol or N-methylo ether groups is accelerated. These are mainly salts of ammonia, amines or polyvalent metals with medium-strength or preferably strong acids; examples are ammonium chloride, ammonium sulfate, ammonium phosphates, ammonium nitrate, dimonoethanolamine hydrogen phosphate, ethanolamine hydrochloride, 2-methyl-2-amino propanol hydrochloride, magnesium chloride, aluminum chloride, zinc chloride and zinc nitrate.

45 It is preferred to use ammonium chloride. The acid catalyst may be used in a smaller amount by weight than the potentially acid catalyst. It has proved to be very suitable to choose a weight ratio between acid catalyst (a) and potentially acid salt (b) in the range of from 1:10 to 1:3. The combination of acid and potentially acid catalyst should be water-soluble; the individual components should not be insoluble in water, nor should an insoluble precipitate form when they are brought together. If it is necessary to use low temperatures, catalyst combinations in which the acid catalyst is present in a smaller amount than the potentially acid catalyst may occasionally give rise to difficulties owing to relatively low solubility. If importance is attached to particularly good solubility of the catalyst combination, it may be more advantageous to choose a combination in which the components (a) and (b) are present in the weight ratio of 1:1 to 5:1, preferably 1:1 to 2:1. The catalyst mixture is preferably used in an amount of 5 to 25% by weight preferably 8 to 25% by weight, based on the weight of crosslinking agent.

In many cases it is advantageous to add to the impregnating liquor, which contains the crosslinking agent and the catalysts, also wetting agents and/or conventional treatment agents for fibrous materials, as for example optical brighteners, water repellants, plasticizers and finishes. Examples of wetting agents are salts of alkyl-naphthalenesulfonic acids, the alkali metal salts of sulfonated dioctyl succinate and adducts of alkylene oxides with fatty alcohols, alkylphenols or fatty amines. Examples of water repellants are known paraffin wax emulsions containing aluminum or zirconium, and also preparations containing silicones and perfluorinated aliphatic compounds. Examples of plasticizers are ethoxylated products of high molecular weight fatty acids, fatty alcohols or fatty acid amides, high molecular weight polyglycol ethers and their esters, high molecular weight fatty acids, fatty alcohol sulfonates, stearyl-N,N-ethylenurea and stearyl amidomethylpyridinium chloride. Examples of finishes which particularly improve the resistance to abrasion of the finished material are cellulose ethers, cellulose esters and alginates, and also solutions or dispersions of synthetic polymers, for example of polyethylene, polyamides, ethoxylated polyamides, polyvinyl ethers, polyvinyl alcohols, polyacrylic acid or esters and amides thereof and also the corresponding polymethacrylic compounds, polyvinyl propionate, polyvinylproline, of copolymers, for example those from vinyl chloride and acrylic esters, butadiene and styrene or acrylonitrile, or from  $\alpha$ -dichloroethylene,  $\beta$ -chloroalkylacrylic esters or vinyl ethyl ether and acrylamide, or the amides of crotonic acid or maleic acid or from N-methylolmethacrylamide and other polymerizable compounds.

It is particularly advantageous to add aqueous dispersions of copolymers of 1 to 25% by weight of a N-methylolamide of an acrylic acid and 99 to 75% by weight of one or more other polymerizable compounds to the impregnating liquor. It has proved to be particularly suitable to use these copolymers in amounts of 5 to 15% on the weight of the crosslinking agent. In this way higher dry crease angles and a better durability of the finish is achieved without detriment to strength.

The material to be treated is impregnated with the impregnating liquor by conventional methods. It is preferred to use a padding machine for the purpose. The impregnated material is freed from excess impregnating liquid in the known manner by squeezing. The liquor retention is preferably correlated to the concentration of the liquor that 5 to 30%, preferably 5 to 20%, by weight of crosslinking agent (on the dry material) remains on the material being treated. Liquor retention is usually from 50 to 100%.

It is very important for the success of the process according to this invention for the impregnated material to be then dried to the correct moisture content, namely to 10 to 35%, preferably 18 to 27%, on the weight of the amorphous region contained in the cellulose. The proportion of the amorphous regions to the total weight is known for the various types of cellulose; in cotton it is for example about 30% and in viscose rayon staple it is about 60%. In the case of cotton it is therefore necessary to dry to a residual moisture content of 3 to 10.5%, preferably 5.5 to 8%, and in the case of viscose rayon staple to a residual moisture content of 6 to 21%, preferably 11 to 16%, in each case on the total amount of cellulose. Drying may be carried out in known manner at temperatures below 130°C. Mixtures of cellulose and other fibres are treated in the same way as pure cellulose fibres of the kind in question. For example, a material consisting of a mixture of cotton fibres and polyester fibres is treated in the same way as a material consisting only of cotton fibres.

When the material has reached the prescribed moisture content, it is stored at a temperature of up to 50°C, preferably at 15° to 35°C, so that the substances having the formula I and/or II can react with the cellulose. The moisture content set up should preferably be prevented from changing appreciably. This may be effected for example by surrounding the material being treated with a moisture-impermeable sheet or by storing it in a chamber whose atmosphere has an appropriate moisture content. Reaction with the cellulose under the said conditions generally takes five to twenty hours. The exact time required may be easily determined by preliminary experiment.

The finished material may be finished off in the conventional way by washing and drying.

Fibrous material which can be finished by the process according to this invention includes fibers, flock, shivers and particularly sheetlike materials, such as non-bonded and bonded non-woven fabrics, woven fabrics, knitted fabrics, and net fabrics. The fibrous material may consist of pure natural or regenerated cellulose fibers, for example cotton, linen, viscose rayon or viscose rayon staple, or of mixtures of these with one

another or with other fibers, for example with wool, silk, cellulose ester fibers or fibers of synthetic polyamides, polyesters polyolefins, acrylonitrile polymers or vinyl chloride polymers.

The present process makes it possible to finish cellulosic fibrous material in a simple and reliable way in a single operation so that they have high to very high wet crease angles of 140° or more and medium dry crease angles of 110° or more. By varying the process conditions it is possible to adapt the size and the difference between the wet and dry crease angles to the requirements in each case. In addition to the said advantages, particularly good abrasion resistance and tensile strength of the material treated can be achieved.

The invention will be further illustrated by the following Examples. The parts and percentages given are by weight unless otherwise stated. Parts by weight bear the same relation to parts by volume as the kilogram to the liter. Determination of the dry crease angle (or dry crease recovery angle) is carried out according to the German Standard DIN 53,890 (see the Standard Specification DIN 53,890 of December 1963 of Deutscher Normenausschuss, Berlin 15).

#### EXAMPLE 1

A bleached and mercerized cotton cloth (poplin) having a weight of 120 g/sq.m. is impregnated by padding with a solution having the following composition:

20 300 parts of a 50% dimethyloolpropyleneurea solution, 20  
 40 parts of a 40% aqueous dispersion of a copolymer of  
 89 parts of n-butylacrylate,  
 5 parts of butanediol diacrylate,  
 3 parts of N-methylolmethacrylamide and  
 25 3 parts of acrylamide,  
 1 part of an adduct of 7 moles of ethylene oxide with 1 mole of isoctylphenyl,  
 3 parts of an optical brightener,  
 3 parts of oxalic acid and  
 10 parts of ammonium chloride

30 is diluted with water to 1000 parts by volume. The liquor retention is 75%.

After the cloth has been impregnated it is dried on a stenter at 110°C to a residual moisture of 7% and rolled up. The roll of cloth is tightly enclosed in a sheet of polyethylene and rotated for sixteen hours at room temperature. The catalyst is then removed by treatment in the cold with alkali and the cloth is washed with soap and soda at 60°C on an open-width washing machine.

35 The cloth is dried and then has the following data; dry crease angle according to DIN 53,890, warp and weft 275°, wet crease angle according to Tootal, warp and weft 305°. After the cloth has been boiled five times in a washing machine, the values are:

40 dry crease angle: warp and weft 270°; 40  
 wet crease angle: warp and weft 300°;  
 Monsanto rating: 5.

#### EXAMPLE 2

45 A cotton cloth is padded as in Example 1 with an impregnating solution having the following composition:

150 parts of a 50% aqueous solution of dimethyloolpropyleneurea, 45  
 150 parts of a 50% aqueous solution of dimethoxymethylurone,  
 40 parts of an aqueous alcoholic solution of an ethenoxylated polyamide;  
 5 parts of monochloroacetic acid and  
 50 30 parts of zinc nitrate,  
 made up with water to a total of 1000 parts by volume.

Drying, dwell and washing are carried out as in Example 1. Technological data of the finish:

55 dry crease angle according to DIN 53,890: warp and weft 260°, 55  
 wet crease angle according to Tootal: warp and weft 290°,  
 after boiling five times in a washing machine:

dry crease angle: 255°;  
 wet crease angle: 288°;  
 Monsanto rating: 4 to 5.

60 A very good finish is also achieved on the material by following the procedure described in Example 1 and using the components and amounts given in the following Examples 3 to 7.

## EXAMPLE 3

Chemicals used per 1000 parts by volume of total liquor:

150 parts of dimethylolethylenurea,  
3 parts of oxalic acid and  
5 10 parts of ammonium chloride.  
Cloth used: cotton poplin, weight 130 g/sq.m.  
Drying carried out at 120°C to 6% residual moisture.  
Dry crease angle: warp and weft 265°;  
wet crease angle: warp and weft 290°.

## 10 EXAMPLE 4

Chemicals used per 1000 parts by volume of total liquor:

130 parts of dimethoxy dimethylurone,  
2.5 parts of oxalic acid and  
15 25 parts of magnesium chloride.  
Cloth used: unbleached cotton cloth, weight 115 g/sq.m.  
Drying carried out at 110°C to 7% residual moisture.  
Dry crease angle: warp and weft 280°;  
wet crease angle: warp and weft 290°.

## 20 EXAMPLE 5

Chemicals used per 1000 parts by volume of total liquor:

175 parts of dimethylolpropylenurea,  
60 parts of a 20% dispersion of a copolyamide (from 40 parts of heptadecane-  
dicarboxylic acid-4,4'-diaminodicyclohexylmethane salt, 20 parts of  
25 caprolactam, 20 parts of capryllactam and 20 parts of hexamethylene  
diamine adipate),  
25 parts of an aqueous dispersion of the copolymer specified in Example 1,  
3.5 parts of oxalic acid and  
10 parts of ammonium chloride.  
Cloth used: cotton stiffening fabric, weight 165 g/sq.m.  
30 Drying carried out at 110°C to 8% residual moisture.  
Monsanto rating: 4 to 5.

## EXAMPLE 6

Chemicals used per 1000 parts by volume of total liquor:

150 parts of dimethylolpropylenurea,  
35 15 parts of an aqueous dispersion of the copolymer specified in Example 1,  
1 part of the adduct of 7 moles of ethylene oxide with 1 mole of isooctylphenol  
(wetting agent),  
10 parts of ammonium chloride and  
3 parts of oxalic acid.  
40 Cloth used: unbleached cotton cloth, weight 145 g/sq.m.  
Drying carried out at 105°C to 10% residual moisture.  
Dry crease angle: warp and weft 300°.  
Wet crease angle: warp and weft 315°.  
Monsanto rating (after washing at 60°C): 4 to 5.

## 45 EXAMPLE 7

Chemicals used per 1000 parts by volume of total liquor:

75 parts of dimethylolethylenurea,  
75 parts of dimethylolgloxal monoureine,  
50 3 parts of oxalic acid and  
25 parts of magnesium chloride.  
Material used: viscose rayon lining, weight 135 g/sq.m.  
Drying carried out at 110°C to 16% residual moisture.  
Monsanto rating (after washing at 40°C): 4 to 5.

## EXAMPLE 8

A bleached and mercerized cotton cloth (poplin) having a weight of 125 g/sq.m. is impregnated by padding with a solution having the following composition:

5      300 parts of a 50% dimethylolethylenurea solution,      5  
       1.2 parts of oxalic acid,  
       5.6 parts of maleic acid,  
       4 parts of ammonium chloride and  
       7 parts of a 25% aqueous solution of an ethenoxylated polyamide  
 10      made up to 1000 parts by volume with water. The liquor retention is 75%.  
       After the cloth has been impregnated it is dried to a residual moisture of 5.5 to  
       6% on a stenter at 110°C and rolled up. The roll of cloth is tightly enclosed with a  
       sheet of polyethylene and rotated for twenty-four hours at room temperature. The  
       catalyst is then removed by treatment in the cold with alkali and the cloth is washed  
       on an open-width washing machine with soap and soda at 60°C.  
 15      The cloth is dried and then has the following technological data:      15  
       dry crease angle (DIN 53,890): warp and weft 260°;  
       wet crease angle (Tootal): warp and weft 300°;  
       loss of tensile strength: 25%.  
 20      If 40 parts of a 40% aqueous dispersion of a copolymer of 89 parts of n-butyl  
       acrylate, 5 parts of butanediol diacrylate, 3 parts of N-methylolmethacrylamide and  
       3 parts of acrylamide is also added to the padding liquor, even better dry and wet crease  
       angles are obtained with the same loss in tensile strength.      20

## EXAMPLE 9

Unbleached cotton cloth which has been dyed with a reactive dye and has a weight of 140 g/sq.m. is impregnated on a padding machine with a solution having the following composition:

25      300 parts of a 50% aqueous solution of dimethylol glyoxal monoureine,      25  
       6.4 parts of ammonium chloride,  
       8.55 parts of maleic acid,  
 30      1.92 parts of oxalic acid,  
       11.4 parts of a 25% aqueous alcoholic solution of an ethenoxylated polyamide,      30  
       made up to 1000 parts by volume with water.  
       The impregnated material is squeezed out to 75% liquor retention, dried with  
       hot air at 120°C to 4.5 to 5% residual moisture and left for twenty-six hours at room  
       temperature, the moisture being prevented from escaping. The catalyst is then re-  
       moved by treatment with alkali in the cold and the cloth is washed with soap and  
       soda at 60°C and dried.  
       The unbleached cloth has the following technological data:  
       dry crease angle: warp and weft 260°;  
 40      wet crease angle: warp and weft 295°;      40  
       Monsanto rating after washing in a washing machine at 90°C: 4 to 5.

## EXAMPLE 10

A coloured viscose rayon staple dress material having a weight of 180 g/sq.m. is impregnated on a padding machine with a liquor having the following composition:

45      100 parts of a 50% aqueous solution of dimethylolethylenurea,      45  
       200 parts of an 85% aqueous paste of N,N'-dimethoxymethylurea,  
       40 parts of the aqueous copolymer dispersion specified in Example 1,  
       4.25 parts of ammonium chloride,  
       5.9 parts of maleic acid,  
 50      1.28 parts of oxalic acid,      50  
       made up with water to 1000 parts by volume.

The impregnated material is squeezed out to a liquor retention of 80%, dried with hot air at 110°C to 13% residual moisture and rolled up. The roll of material is tightly enclosed in a sheet of polyethylene and rotated for thirty hours at room temperature. The catalyst is then removed by treatment with alkali in the cold and the cloth is washed with soap and soda at 60°C on an open-width washing machine and dried. 5

The finished cloth has the following technological data:

dry crease angle: warp and weft 240°;

wet crease angle: warp and weft 300°.

After a washing b (DIN 54,010) the values are: 10

dry crease angle: warp and weft 230°;

wet crease angle: warp and weft 295°.

#### EXAMPLE 11

A cotton imitation poplin cloth (the difference between true poplin and imitation poplin being the fact that in true poplin both the warp and weft fibers are twisted, whereas in imitation poplin only the warp fibers are twisted, and the weft fibers consist of untwisted yarn) having a weight of 120 g/sq.m. is impregnated with a liquor having the following composition: 15

300 parts of a 50% aqueous solution of dimethylolpropyleneurea,

30 parts of a 40% aqueous dispersion of a copolymer of 95 parts of n-butyl 20

acrylate and 5 parts of N-methylolmethacrylamide,

6.65 parts of a 25% aqueous alcoholic solution of an ethoxylated polyamide,

3.7 parts of ammonium chloride,

5.2 parts of maleic acid,

1.12 parts of oxalic acid,

25 made up to 1000 parts by volume with water.

The impregnated material is squeezed out to 70% liquor retention, dried at 105° to 110°C to 6% residual moisture and rolled up. The roll is tightly enclosed in a polyethylene sheet and rotated for twenty-four hours at 35°C. The catalyst is then removed with an aqueous alkaline liquor and the cloth is washed and dried. 25

The finished cloth has the following technological data: 30

dry crease angle: warp and weft 250°;

wet crease angle: warp and weft 290°.

After the finished cloth has been washed once at the boil in a washing machine, 35

the values are:

dry crease angle: warp and weft 245°;

wet crease angle: warp and weft 290°;

Monsanto rating: 4.5.

If the same procedure is followed except that the copolymer dispersion is replaced by 50 parts of a 50% aqueous dispersion of a copolymer of 53.8 parts of n-butyl acrylate, 44.1 parts of vinyl acetate and 2.1 parts of acrylic acid, the cloth has 40

the following technological data:

dry crease angle: warp and weft 240°;

wet crease angle: warp and weft 275°.

After the finished cloth has been washed once at the boil in a washing machine, 45

the values are:

dry crease angle: warp and weft 220°;

wet crease angle: warp and weft 280°;

Monsanto rating: 4.

#### EXAMPLE 12

A cotton cloth (material for bed-sheets) having a weight of 200 g/sq.m. is impregnated on a padding machine with a liquor having the following composition: 50

350 parts of a 90% aqueous solution of 1,3-dimethylol-5-isobutyl-triazinone-2,

9.5 parts of a 25% aqueous alcoholic solution of an ethoxylated polyamide,

5.3 parts of ammonium chloride,

7.4 parts of maleic acid and

1.6 parts of oxalic acid

55 made up to 1000 parts by volume with water.

The impregnated material is worked up as described in Example 9. It has the following technological data:

60 dry crease angle: warp and weft 240°;

wet crease angle: warp and weft 310°.

After one washing at the boil in a washing machine:  
dry crease angle: warp and weft 230°;  
wet crease angle: warp and weft 300°;  
Monsanto rating: 5.

**EXAMPLE 13**

**EXAMPLE 15**  
A cambric of 50% of cotton and 50% of polyglycol terephthalate ester fibers having a weight of 110 g/sq.m. is impregnated with a liquor having the following composition:

10 320 parts of a 50% aqueous solution of N-dimethoxymethylethylurethane (= N-dimethoxymethylcarbamic acid ethyl ester),  
 10.5 parts of a 25% aqueous alcoholic solution of an ethenoxylated polyamide,  
 5.8 parts of ammonium chloride,  
 8.1 parts of maleic acid and  
 1.8 parts of oxalic acid  
 15 made up to 1000 parts by volume with water.

The impregnated material is worked up as described in Example 9. It has the following technological data:  
dry crease angle: warp and weft 300°.

After the cloth has been washed for twenty minutes in a washing machine at  $60^{\circ}\text{C}$ , these values are unchanged.

If the N-dimethoxymethyl ethylurethane be replaced by the same amount of N,N'-dimethylolbutanediol-1,4-diurethane or N,N'-tetramethylolbutanediol-1,4-diurethane under otherwise the same procedure, the same values are obtained.

**EXAMPLE 14**

**EXAMPLE 14**  
The cloth specified in Example 11 is impregnated with a liquor having the following composition:

300 parts of a 50% aqueous solution of dimethylolpropyleneurea,  
6.65 parts of a 25% aqueous alcoholic solution of an ethoxylated polyamide,  
3.7 parts of ammonium chloride,  
5.2 parts of maleic acid and  
1.12 parts of oxalic acid

35 made up to 1000 parts by volume with water. The impregnated material is worked up as described in Example 11. It has the following technological data:  
dry crease angle: warp and weft 245°;  
wet crease angle: warp and weft 280°;  
tear resistance according to Elmendorf: 750 g.

After having been sewn, the material exhibits five points of thread breakage in 1 meter of sewn length.

If the same procedure is followed except that 30 parts of a 30% aqueous dispersion of polyethylene is added to the impregnating liquor, the following values are obtained:

45 dry and wet crease angles: unchanged;  
tear resistance according to Elmendorf: 900 g;  
0.9 points of thread breakage in 1 meter of length sewn.

**EXAMPLE 15**

A cotton imitation poplin cloth having a weight of 120 g/sq.m. is impregnated with a liquor having the following composition:

50 300 parts of a 50% aqueous solution of dimethylolpropylenurea,  
12 parts of phosphoric acid and  
3.2 parts of ammonium sulfate  
made up with water to 1000 parts by volume.

55 The impregnated material is squeezed out to 70% liquor retention and dried to a residual moisture of 7%. It is then rolled up and the roll is turned at 20°C for twenty-four hours, the moisture being prevented from escaping. The catalyst is then removed with an aqueous alkaline liquor and the cloth is then washed and dried.

It has the following technological data:  
60 dry crease angle: warp and weft  $280^\circ$ ;  
wet crease angle: warp and weft  $310^\circ$ .

## EXAMPLE 16

The cloth specified in Example 15 is impregnated with a liquor having the following composition:

300 parts of a 50% aqueous solution of dimethylolpropylenurea,

5 4 parts of sulfuric acid,

20 parts of 2-methyl-2-aminopropanol hydrochloride

and made up with water to 1000 parts by volume.

The impregnated cloth is squeezed out to 70% liquor retention and dried to 4% residual moisture. It is then rolled up and the roll is rotated for twenty-four hours at 20°C, the moisture being prevented from escaping. Further working up is carried out as described in Example 15.

The cloth has the following technological data:

dry crease angle: warp and weft 270°;

wet crease angle: warp and weft 300°.

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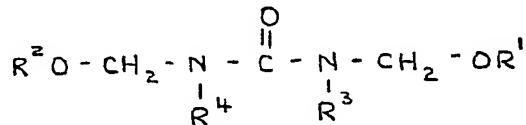
## WHAT WE CLAIM IS:—

1. A process for finishing cellulosic fibrous material with a monomeric compound which contains at least two groups having the formula  $-\text{CH}_2\text{OR}$  (in which R denotes a hydrogen atom or a low molecular weight alkyl radical as hereinbefore defined) attached to the nitrogen atom of a carbamide group, as hereinbefore defined, as cross-linking agent, wherein the material is impregnated with an aqueous solution or dispersion which contains at least one crosslinking agent of the said type and a water-soluble catalyst comprising a mixture of:

(a) at least one strong or medium-strength acid, as hereinbefore defined, which is not volatile at temperatures up to 130°C and

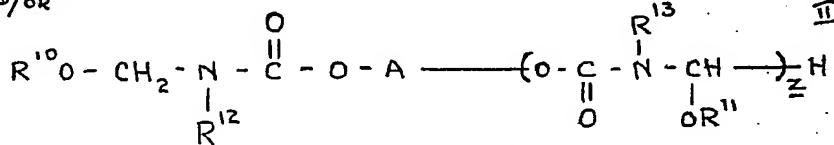
(b) at least one potentially acid salt, the ratio by weight of (a) to (b) being from 1:10 to 5:1, the impregnated material is dried to a moisture content of the cellulose of 10 to 35% by weight, with reference to the weight of the amorphous regions contained in the cellulose, and allowed to react with the applied crosslinking agent at a temperature of up to 50°C.

2. A process as claimed in claim 1 wherein the crosslinking agent used has one of the formulae I and II:



I

AND/OR

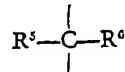


II

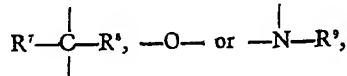
in which z denotes zero or 1, R<sup>1</sup>, R<sup>2</sup>, R<sup>10</sup> and R<sup>11</sup> are identical or different and denote hydrogen atoms or low molecular weight alkyl groups as hereinbefore defined, R<sup>1</sup> and R<sup>2</sup> may be identical or different and denote radicals having the formula

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which are connected together directly or via radicals



or when R<sup>1</sup> and R<sup>2</sup> denote low molecular weight alkyl radicals, may also denote hydrogen atoms, low molecular weight alkyl groups or low molecular weight alkoxy-methyl groups as hereinbefore defined, R<sup>5</sup> and R<sup>7</sup> denote hydrogen atoms, R<sup>6</sup> and R<sup>9</sup>

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may be identical or different and denote hydrogen atoms, hydroxyl groups, low molecular weight alkyl groups or low molecular weight alkoxy groups as hereinbefore defined,  $R^0$  denotes a hydrogen atom, a low molecular weight alkyl group or a low molecular weight hydroxyalkyl group as hereinbefore defined,  $R^{12}$  denotes a hydroxymethyl group or a low molecular weight alkoxyethyl group as hereinbefore defined if  $z$  is zero, and a hydrogen atom, a hydroxymethyl group or a low molecular weight alkoxyethyl group as hereinbefore defined if  $z$  is 1,  $R^{13}$  denotes a hydrogen atom, a hydroxymethyl group or a low molecular weight alkoxyethyl group as hereinbefore defined, and A denotes a divalent aliphatic hydrocarbon radical having two to eight carbon atoms.

3. A process as claimed in claim 1 or 2 wherein the catalyst mixture is used in an amount of 8 to 25% by weight based on the weight of crosslinking agent.

4. A process as claimed in any of claims 1 to 3 wherein an aqueous dispersion of a copolymer of 1 to 25% by weight of a N-methylolamide of an acrylic acid and 99 to 75% by weight of one or more other polymerizable compounds is added to the impregnating liquor.

5. A process as claimed in claim 4, wherein the copolymer is added in an amount of 5 to 15% on the weight of the substance having formula I or II.

6. A process as claimed in any of claims 1 to 5 wherein the impregnated material is dried to a moisture content of 18 to 27% by weight with reference to the weight of the amorphous regions contained in the cellulose.

7. A process as claimed in any of claims 1 to 6 wherein the impregnated and partly dried material is allowed to react at a temperature of 15° to 35°C with the applied crosslinking agent.

8. A process as claimed in any of claims 1 to 7 wherein an ethenoxylated polyamide is added to the impregnating liquor.

9. A process according to claim 1 for finishing cellulosic fibrous material carried out substantially as described in any of the foregoing Examples.

10. Cellulosic fibrous material which has been finished by a process as claimed in any of claims 1 to 9.

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